CHM 305 - Lecture 4 - The Free Particle & A Particle in a Box

Prof. Marissa Weichman

We have now discussed classical waves and introduced Schrödinger's quantum mechanical wave equation. Today we will work through some examples of quantum particles evolving in time according to the Schrödinger equation on very simple potential surfaces. In particular, today we will cover the free particle and the particle-in-a-box (PIB), which are useful model systems for how electrons behave in free space and when confined in a molecular π-bonding network or a quantum dot.

In the following lectures we will dive into the so-called postulates (e.g. the rules of the game) of quantum mechanics, using today's results as tangible examples. This material is also covered nicely in McQuarrie Chapter 3 and Griffiths Chapter 2.

1 A Brief Roadmap for Solving the Schrödinger Equation

Let's quickly summarize what we covered last class, and write down a roadmap for how we will approach nearly every problem we encounter in quantum mechanics.

Our job is to solve the Schrödinger equation to find the wavefunction $\Phi(x,t)$ which gives us a probability distribution for where we expect to find the particle at any particular time as it explores some potential $V(x)$. We will often be given some initial condition of the system, $\Phi(x,t=0)$.

1. **Write down** $V(x)$: For a given problem, we will consider a time invariant potential $V(x)$. The potential might be very simple, like $V(x)=0$ for the free particle, or it might have a more complex form which leads to interesting emergent phenomena like $V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$ for the hydrogen atom in 3D space (where r is the distance between electron and proton).

2. **Write down the TISE**: We will write down the time-*independent* Schrödinger equation (TISE) by plugging in the appropriate $V(x)$:

$$\hat{H}\psi_n(x) = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi_n(x) = E_n\psi_n(x) \tag{1}$$

3. **Solve the TISE for** $\{\psi_n(x)\}$ **and** $\{E_n\}$**:** Solve the equation above to find our stationary-state spatial solutions, $\{\psi_n(x)\}$, labeled with index n, and each with their own associated energy $\{E_n\}$.

4. **Write down the temporal parts of the stationary states** $\{\phi_n(t)\}$: Once we have our $\{E_n\}$ we can immediately write down the corresponding temporal components of the wavefunction, $\{\phi_n(t)\}$. We know how to do this since we solved for the time-dependence of stationary states last lecture:

$$\phi_n(t) = e^{-iE_nt/\hbar} \tag{2}$$

5. **Write down the complete stationary state wavefunctions** $\{\Psi_n(x,t)\}$: We can write down each stationary state wavefunction in its full spatial and temporal glory as:

$$\Psi_n(x,t) = \psi_n(x) \cdot \phi_n(t) \tag{3}$$
$$= \psi_n(x) \cdot e^{-iE_n t/\hbar} \tag{4}$$

6. **Write down the general wavefunction** $\{\Phi(x,t)\}$: We can finally write down the general solution as a linear combination of our basis set of stationary states:

$$\Phi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x)\phi_n(t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar} \tag{5}$$

7. **Determine the** c_n **coefficients for** $\{\Phi(x,t)\}$: We will learn how to choose the c_n coefficients so that $\Phi(x,t)$ satisfies some given initial condition like $\Phi(x,t=0)$.

We will work our way through this roadmap for two simple systems in today's lecture.

2 One Quick Word on Wavefunction Notation

I try to use the following system for notating wavefunctions, for consistency, and so it's easier to understand what a wavefunction means at a glance.

Lowercase $\psi(x)$:

- $\psi(x)$: spatial part of a wavefunction
- $\psi_n(x)$: spatial part of a stationary state solution to the Schrödinger equation with index n

Lowercase $\phi(t)$:

- $\phi(t)$: temporal part of a wavefunction
- $\phi_n(t)$: temporal part of a stationary state solution to the Schrödinger equation with index n

Uppercase $\Psi(x,t)$:

- $\Psi(x,t)$: a complete temporal and spatial description of a wavefunction
- $\Psi_n(x,t)$: a complete temporal and spatial description of a stationary state solution to the Schrödinger equation with index n

$$\Psi_n(x,t) = \psi_n(x) \cdot \phi_n(t) = \psi_n(x)\, e^{-iE_n t/\hbar} \tag{6}$$

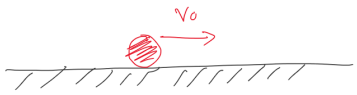
Uppercase $\Phi(x,t)$:

- $\Phi(x,t)$: a complete temporal and spatial description of an arbitrary wavefunction. This wavefunction will solve the Schrödinger equation but may not be a stationary state, since in general a linear combination of stationary states won't factor neatly into spatial and temporal parts.

$$\Phi(x,t) = \sum_{n=1}^{\infty} c_n \Psi_n(x,t) = \sum_{n=1}^{\infty} c_n\, \psi_n(x)\, e^{-iE_n t/\hbar} \tag{7}$$

3 The Free Particle

Let's dive in to solving for the quantum behavior of a simple system. The simplest system that we can imagine that of a free particle, which can travel along the x axis, with no forces acting on it. Classically, we might think of a free particle as a frictionless billiard ball rolling on flat ground:



From Newton's laws we know that for the classical system:

$$F = m \cdot a = m \cdot \frac{d^2x}{dt^2} = 0 \tag{8}$$

And therefore that the equation of motion for this classical ball is motion at a constant velocity

$$x = x_0 + v_0 \cdot t \tag{9}$$

where x_0 is the ball's initial position at time $t = 0$ and v_0 is its initial velocity.

With this classical context in mind, we can turn to the quantum mechanical free particle. We actually already touched on this system in our motivation of the Schrödinger equation, but it won't hurt to go over it again. The potential energy surface is flat, so we can set $V(x) = 0$.

3.1 Find the free particle's spatial wavefunctions

We can now write down the time-independent Schrödinger equation and solve for the spatial components of the free particle stationary state wavefunctions:

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x) \tag{10}$$

We are therefore working with the following differential equation, when rearranged:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) \tag{11}$$

We have already solved differential equations very much like this one, so we have a good idea about functions $\psi(x)$ that return themselves times a constant when differentiated twice. We know for instance, that $\sin(kx)$ and $\cos(kx)$ will work, provided k is chosen correctly.

It will turn out to be convenient, however, to instead use the complex exponential form for our solutions to Eqn. 11:

$$\psi_k(x) = Ae^{ikx} \tag{12}$$

We also need to find an expression for k. By plugging our guess of Eqn. 12 into Eqn. 11, we find

$$k = \pm\sqrt{\frac{2mE}{\hbar^2}} = \pm\frac{1}{\hbar}\sqrt{2mE} = \pm\frac{p}{\hbar} = \pm\frac{2\pi}{\lambda_D} \tag{13}$$

which should look familiar. This is our old friend the wavevector, which we can relate to the particle's momentum and its de Broglie wavelength. Note that I've used the fact that with $V(x) = 0$ for all x, the total energy of the system is just the kinetic energy and we have:

$$E = E_{KE} = \frac{p^2}{2m} \tag{14}$$

To sum up, for clarity, our spatial solutions for this system and their corresponding energies are

$$\boxed{\psi_k(x) = Ae^{ikx}, \quad E_k = \frac{\hbar^2 k^2}{2m}} \tag{15}$$

We use k as our quantum number to label each of these solutions, though it is a continuous quantity that can take any real value between $-\infty$ and $+\infty$. An important note is that this differential equation does not constrain the value of k. The particle's kinetic energy E can take on any real positive value, and therefore any real value of the wavevector k is allowed.

3.2 Putting it all together with the free particle's temporal evolution

Our final step is to consider the time-dependence of the free particle's stationary state wavefunctions. We can always immediately write down the time-dependence of a stationary state with energy E_k as:

$$\phi_k(t) = e^{-iE_k t/\hbar} \equiv e^{-i\omega_k t} \tag{16}$$

where $\omega_k \equiv E_k/\hbar$.

We can therefore write out each total free particle wavefunction as:

$$\Psi_k(x,t) = \psi_k(x)\,\phi_k(t) = \psi_k(x)\,e^{-i\omega_k t} = A\,e^{i(kx-\omega_k t)} \tag{17}$$

These are simply traveling plane waves, moving either to the right or left, at a constant velocity $v = \omega_k/k$, just like classical traveling waves. In fact, this is the exact quantum wave that we started with at the beginning of last class, which we used to motivate the Schrödinger equation.

Let's try to draw some connections between the classical and quantum mechanical free particles:

- both travel along x at a constant velocity
- their allowed momenta and kinetic energies are continuous – all real values are allowed.

It will turn out momentarily that once we start to *confine* the particle to some region of space the allowed energies will become discrete.

Note: It's also worth recalling here how to write down the general wavefunction given by a linear combination of stationary states, since we have a continuous set of basis functions here rather than discrete ones. Instead of writing the linear combination as a sum over discrete indexes n, we can write an integral over all real k:

$$\Phi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i\omega_n t} \qquad \text{discrete} \tag{18}$$

$$\Phi(x,t) = \int_{-\infty}^{+\infty} c(k)\,\psi_k(x) e^{-i\omega t}\,dk = \int_{-\infty}^{+\infty} c(k)\,e^{i(kx-i\omega_k t)}\,dk \qquad \text{continuous} \tag{19}$$

Here $c(k)$ is a continuous function which captures the relative weighting of the component with wavevector k. This turns out to be a continuous Fourier transform, and there are very tidy mathematical ways to find $c(k)$ given the initial condition $\Phi(x, t = 0)$.

Using these linear combinations of continuous waves allows you to construct various interesting solutions, including "wavepackets," which trade certainty in the wavevector for spatial localization. We won't get into this here, but will return to this idea when we discuss quantum uncertainty in a few lectures. Griffiths Chapter 2 covers more on this topic, for those interested.

3.3 Practice Problem 1

We found that a stationary state of the free particle Hamiltonian might look like:

$$\psi_k(x) = Ae^{-ikx} \tag{20}$$

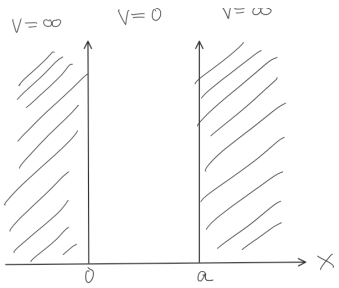
where $k = (2mE)^{1/2}/\hbar$.

We will require that the energy of the system E be a positive real number. Let's consider why this is. What would go wrong if E is allowed to take on a negative value?

4 Particle in a 1D Box

The particle-in-a-box is the next simplest system we can consider. Its solution will look familiar, from when we considered the wavefunction for a guitar string with the boundary condition that it is fixed at both ends. So, let's imagine that we have a quantum particle confined to a 1-dimensional region of space, for x in the window $[0, a]$. To do this, we will define $V(x)$ as:

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & \text{elsewhere} \end{cases}$$



Again, let's follow our procedure of writing down the time-independent Schrödinger equation in order to solve for the stationary state wavefunctions:

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{21}$$

$$\rightarrow \frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2}\Big[V(x) - E\Big]\psi(x) \tag{22}$$

Outside of the box, for $x < 0$ and $x > a$, we have $V(x) = \infty$. Given Eqn. 22, this would cause $\frac{d^2\psi(x)}{dx^2} \to \infty$. This would make our wavefunction very badly behaved. We can salvage this situation by setting $\psi(x) = 0$ for all x outside the box, to kill the exploding potential on the righthand side of Eqn. 22. We will also require $\psi(x)$ to be continuous for all x (for reasons we will learn next class).

This leads us to the following boundary conditions at the edges of the box:

$$\boxed{\psi(0) = \psi(a) = 0} \tag{23}$$

which look an awful lot like the boundary conditions we had for the guitar string!

Inside the box, for $0 \leq x \leq a$, we have $V(x) = 0$, and Eqn. 22 will behave exactly the same as the free-particle Schrödinger equation. With $V(x) = 0$, Eqn. 22 becomes:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) \tag{24}$$

Our solution will be very similar to what we did above for the free particle, except that we are now subject to boundary conditions. Let's write down a general solution to work from, this time using sine and cosine functions for convenience instead of complex exponentials:

$$\psi(x) = Ce^{ikx} + De^{-ikx} = A\sin(kx) + B\cos(kx) \qquad \text{for } 0 \leq x \leq a \tag{25}$$

where we again have our friend the wavevector, $k = \sqrt{2mE/\hbar^2}$. Note that A, B, C, and D may be complex.

We can now constrain A, B, and k using our boundary conditions:

$$\psi(0) = 0 = A\sin(0) + B\cos(0) = 0 + B \;\; \to \;\; \boxed{B = 0} \tag{26}$$

$$\psi(a) = A\sin(ka) = 0 \;\; \to \;\; \boxed{ka = \pi n, \quad \text{for } n = 1, 2, \ldots} \tag{27}$$

This should again look very familiar from the guitar string problem. We see the emergence of ***quantization*** of k where it takes on specific discrete values:

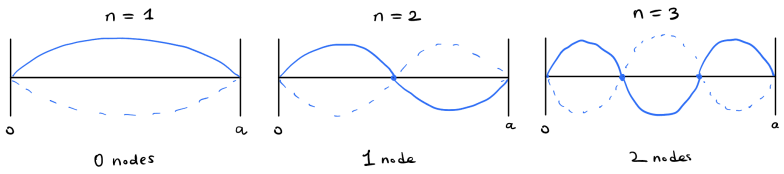
$$\boxed{k = \frac{\pi n}{a} \;\; \text{for } n = 1, 2, \ldots} \tag{28}$$

Plugging this value of k back into our expression for $\psi(x)$, and setting $B = 0$ we arrive at:

$$\boxed{\psi_n(x) = A\sin\left(\frac{n\pi x}{a}\right) \;\; \text{for } n = 1, 2, \ldots} \tag{29}$$

These are our 1D PIB spatial wavefunctions – though we have not yet determined the proper normalization coefficient A, a problem we will return to later on. Note also that we do not include $n = 0$, as this simply results in the trivial solution with $\psi(x) = 0$ for all x (meaning that there is no particle to be found in our box).

Each of these wavefunctions come associated with a specific k, and therefore a specific energy. We would also like to write down these special values of energy. We already know that the wave



vector k is quantized, and we know its relationship to kinetic energy from our work with the free particle. So the quantized energies E_n corresponding to each stationary state $\psi_n(x)$ are:

$$\boxed{E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{\pi n}{a}\right)^2 \propto n^2 \qquad n = 1, 2, \ldots} \tag{30}$$

You can check that these energy values do indeed yield solutions to the time-independent Schrödinger equation by verifying that $\hat{H}\psi_n(x) = E_n\psi_n(x)$ for each integer n. We call this integer index n the "quantum number." By specifying n, we determine both the spatial wavefunction $\psi_n(x)$ and its energy E_n.

For completeness, let's recall that if we were writing down the complete spatial and temporal wavefunction for our stationary states, we would write:

$$\Psi_n(x,t) = \psi_n(x)\,\phi_n(t) = \psi_n(x)\,e^{-iE_nt/\hbar} \tag{31}$$

And a general, arbitrary solution would look like:

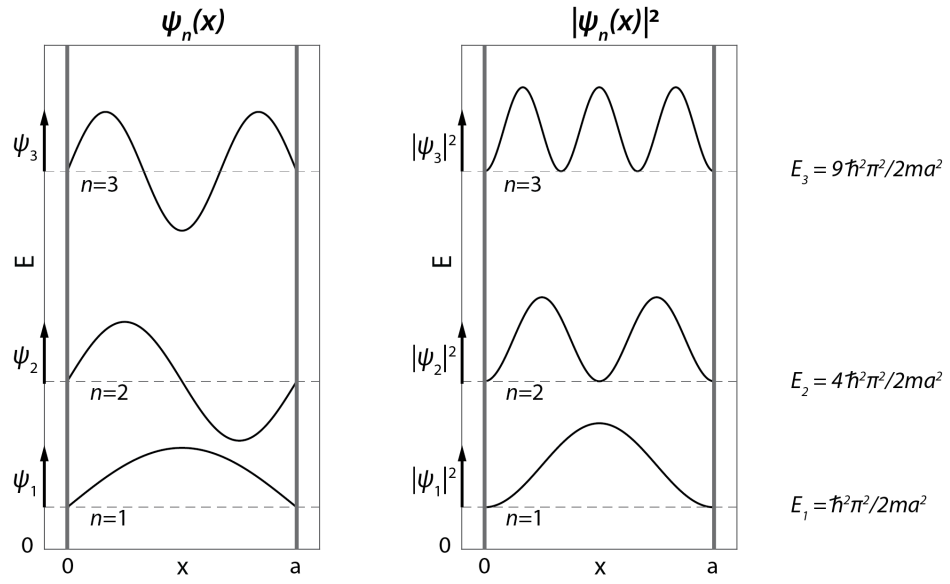
$$\Phi(x,t) = \sum_n c_n\psi_n(x)\,e^{-iE_nt/\hbar} \tag{32}$$

Note that these basis states form a *discrete* basis, as opposed to the continuous basis we had for the free particle system.

Let's plot our stationary state spatial wavefunctions, again alongside the probability densities for each wavefunction, which are proportional to $|\psi(x)|^2$. It's also nice to plot the spatial structure of the wavefunctions vertical offset by the energy of each state.

We notice several interesting things looking at these plots:

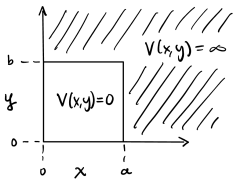
- These are the wavefunctions that do indeed meet the boundary conditions, such that exactly an integer number of half-wavelengths fit in the box.
- The wavefunctions have nodes at fixed positions, which are independent of time. The number of nodes is closely related to the quantum number: for the n^{th} solution we always see $n-1$ nodes. Higher energy wavefunctions always carry more nodes.
- The energy of the lowest energy wavefunction features $E_1 > 0$. This is called the *zero point energy*. A confined quantum particle in it's ground state will always have finite energy, which we call the "zero point energy." You can think of this as the energy penalty we pay for insisting that the particle be confined to its box.
- A particle in each of these states is delocalized, as shown by the probability densities. For instance, in the lowest energy state, all we know about the particle's position is that we expect it to be more likely to be found in the center of the box rather than near the edges.



5 Particles in Boxes of Higher Dimension

The PIB generalizes quite simply from one dimension towards higher dimensions. Let's build there gradually. If we consider 2D space, we can think about a box of width a along the x axis and width b along the y axis:

$$V(x,y) = \begin{cases} 0 & 0 \leq x \leq a \\ 0 & 0 \leq y \leq b \\ \infty & \text{elsewhere} \end{cases} \tag{33}$$



Inside the box, where $V = 0$, the time-independent Schrödinger equation in two spatial dimensions looks like:

$$\hat{H}\psi(x,y) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi(x,y) = E\psi(x,y) \tag{34}$$

Let's search for spatial stationary state solutions that factor into x and y components, e.g. $\psi(x,y) = A \cdot X(x) \cdot Y(y)$. If we plug this form of $\psi(x,y)$ into Eqn. 34, then we find that we can break the differential equation into two halves using separation of variables in x and y. This exercise is left to the reader, but if you carry it out, you will find that you have two independent 1D PIBs with two independent quantum numbers, n and q, that describe the number of nodes along the x and y

axes respectively:

$$X_n(x) = \sin\left(\frac{n\pi x}{a}\right) \tag{35}$$

$$Y_q(y) = \sin\left(\frac{q\pi y}{b}\right) \tag{36}$$

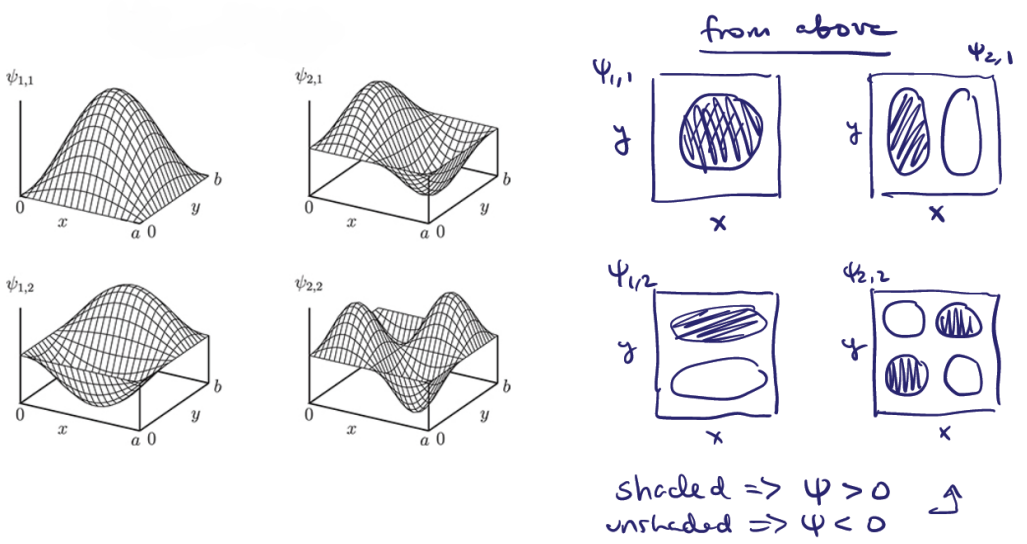
$$\psi_{nq}(x,y) = A \cdot X_n(x) \cdot Y_q(y) = A \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{q\pi y}{b}\right) \tag{37}$$

The total energy of the system is simply the sum of the two independent 1D PIB energies:

$$E = E_x + E_y = \frac{\hbar^2\pi^2}{2m}\left[\frac{n^2}{a^2} + \frac{q^2}{b^2}\right] \tag{38}$$

It is generally true that if the wavefunction factors into independent components, the energy of the system will be a sum of the energies of those independent components. What we've done here for the 2D PIB generalizes to any higher dimension.

We can sketch what a few of these wavefunctions might look like, e.g. where are the nodes?



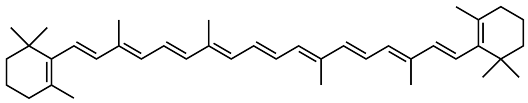
6 Real Examples

Finally, let's discuss a few real-world examples that can be approximated by a PIB.

6.1 Extended aromatic molecules

The electrons living in the π bonds of extended conjugated molecules can be treated as 1D PIBs: they are delocalized along the single dimension of the conjugated network of bonds, while accessing any other region of space is energetically unfavorable (e.g. $V \to \infty$).

Consider the molecule β-carotene:



This molecule has a conjugated region that is approximately 2.4 nm long and contains 11 π bonds. There are therefore 22 π electrons filling the lowest 11 orbitals of the π network, because two electrons of opposite spin fit in each orbital. Can we write down an expression for the lowest-energy electronic transition of β-carotene? The lowest energy transition will promote an electron from a $n_1 = 11$ level, to the next level, $n_2 = 12$. We will simply use our expression for 1D PIB energies:

$$\Delta E = E_{n_2} - E_{n_1} = \frac{\hbar^2 \pi^2}{2ma^2}(n_2^2 - n_1^2) \tag{39}$$

6.2 Quantum dots

Quantum dots are nanoscale objects, typically spheres of a few nanometers in diameter, made out of a semiconductor material like CdSe. An electron in a quantum dot experiences quantum confinement in three dimensions, and can be thought of as a 3D PIB.

The energy it takes to excite an electron in a quantum dot can be modeled as a 3D PIB, which means that the colors of light that a quantum dot absorbs depends on its size. As an example, let's get a little more explicit and approximate an electron residing in our quantum dot as a particle-in-a-cube with side lengths d. The ground state of our electron is labeled with three quantum numbers as $(n_x, n_y, n_z) = (1, 1, 1)$. The next lowest-energy states feature an addition of one node along one of these three dimensions, $(n_x, n_y, n_z) = (1, 1, 2), (1, 2, 1), (2, 1, 1)$. The transition energy between these two states is therefore:

$$\Delta E = E_{112} - E_{111} = \frac{\hbar^2 \pi^2}{2md^2}\left[(1^2 + 1^2 + 2^2) - (1^2 + 1^2 + 1^2)\right] = \frac{3\hbar^2 \pi^2}{2md^2} \propto \frac{1}{d^2} \tag{40}$$

Because the transition energies $\Delta E \sim 1/d^2$, where d is the diameter, the smaller the dot, the more energy needed to excite an electron, and the bluer the light the dot will absorb.

